JC07 Rec'd PCT/PTO 22 JAN 2002

FORM PTO 1390 (REV. 11-2000)

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY DOCKET NUMBER
2534-00066

U S APPLICATION NO (if known, see 37 CFR 1 5)
10/031739

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FI00/00585	**28 June 2000**	**21 July 1999**

TITLE OF INVENTION
A Comonomer, and a Polymer Stabilized with it During Polymerization

APPLICANT(S) FOR DO/EO/US
Markku Auer, Carl-Erik Wilén, Juha Strandén, Ari Rosling, Jan Näsman (deceased) and Hendrik Luttikhedde

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☒ is attached hereto (required only if not communicated by the International Bureau).
   b. ☐ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☐ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a ☒ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ☐ A English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:
    ☒ International Preliminary Examination Report.
    ☒ Supplement to Transmittal Letter .

JC13 Rec'd PCT/PTO 22 JAN 2002

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/031739	PCT/FI00/00585	2534-00066

21. ☒ The following fees are submitted:

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.....		$ 1,040.00
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....	$	890.00
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	$	740.00
International preliminary examination fee (37 CFR 1.482).paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)..	$	710.00
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims satisfied provisions of PCT Article 33(1)-(4).....	$	100.00

CALCULATIONS PTO USE ONLY

ENTER APPROPRIATE BASIC FEE AMOUNT = **$1,040.00**

Surcharge of $130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 C.F.R. 1.491(3)). +

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total Claims	32 - 20 =	12	x $ 18.00	**$216.00**
Independent Claims	5 - 3 =	2	x $ 84.00	**$168.00**
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $280.00	**-0-**

TOTAL OF ABOVE CALCULATIONS = **$1,424.00**

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. **-0-**

SUBTOTAL = **$1,424.00**

Processing fee of $130.00 for furnishing the English Translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 C.F.R. 1.492(f)). **-0-**

TOTAL NATIONAL FEE = **$1,424.00**

Fee for recording the enclosed assignment (37 C.F.R. 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. 3.28, 3.31). **$40.00** per property **-0-**

TOTAL FEES ENCLOSED = **$1,424.00**

Amount to be refunded:

Charged:

~~The PTO did not receive the following~~ listed item(s)
Only $ 1124

a. ☒ A check in the amount of **$1,424.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of $_____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **01.200** . A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:
ANDRUS, SCEALES, STARKE & SAWALL, LLP
100 East Wisconsin Avenue, Suite 1100
Milwaukee, Wisconsin 53202
Phone: (414) 271-7590
Fax: (414) 271-5770

Thomas M. Wozny — Signature — January 21, 2002 — Date

Thomas M. Wozny — Name — 28,922 — Reg. No.

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/031739	**PCT/FI00/00585**	**2534-00066**

CERTIFICATE OF EXPRESS MAIL

I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as EXPRESS MAIL-POST OFFICE TO ADDRESSEE, in an envelope addressed to: BOX PCT, COMMISSIONER OF PATENTS AND TRADEMARKS, WASHINGTON, D.C. 20231 on **January 21, 2002**. Express Mail Label **EL812733606US**.

Dorothy A. Hauser

Dorothy A. Hauser

January 21, 2002

Date

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:

Markku Auer
Carl-Erik Wilén
Juha Strandén
Ari Rosling
Jan Näsman (deceased)
Hendrik Luttikhedde

Filed Herein

Int'l App. No. PCT/FI00/00585

Priority Date: July 21, 1999

A COMONOMER, AND A POLYMER STABILIZED WITH IT DURING POLYMERIZATION

CERTIFICATE OF EXPRESS MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as EXPRESS MAIL in an envelope addressed to: Commissioner of Patents Washington, D.C. 20231 on this 21st day of January, 2002. The Express Mail Label is EL812733606US.

January 21, 2002
Dorothy A. Hauser Date

PRELIMINARY AMENDMENT

Box: PCT
Commissioner of Patents
Washington, D.C. 20231

Sir:

In the matter of the above-identified patent application, please enter the following:

IN THE SPECIFICATION:

The following heading and paragraph at page 1 have been added between the title and the first line of text as follows:

CROSS-REFERENCE TO RELATED APPLICATIONS

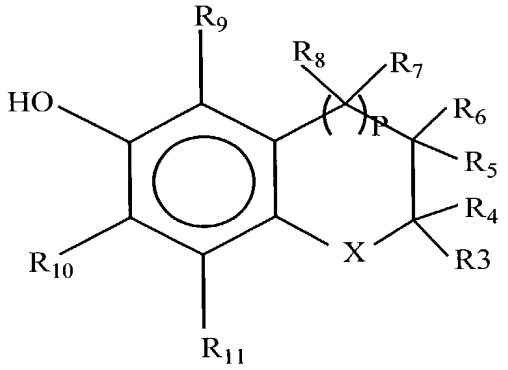
This application is the U.S. national stage application of International Application PCT/FI00/00585, filed June 28, 2000.

Please add an "Abstract", attached to this Preliminary Amendment as new page 34.

IN THE CLAIMS:

Please amend claims 1, 4-14, 20-23, and 26-32.

1. (Amended) E-vitamin derivative or a compound analogous with it, having the formula (I)



(I)

where X is an oxygen or sulfur atom, p is an integer 0 to 1, and R_3-R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II)

$$-(CH_2)_n-(CR_1R_2)_m-(CH_2)_o-CH=CH_2 \qquad (II)$$

where n, m and o are integers 0-4 independent of each other and m+n+o is an integer 1-6 and R_1 and R_2 are identical or different groups selected from hydrogen or C_{1-6}alkyl or C_{1-6}alkene, which may be substituted with an aromatic ring,

or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene.

4. (Amended) Derivative as defined in claim 1, characterized in that one of groups R_3 and R_4 or one of groups R_5 and R_6 is hydrogen or a C_{1-6}alkyl and the other an α-alkene consistent with formula (II) and R_7-R_{11} are hydrogens or C_{1-6}alkyls.

5. (Amended) Derivative as defined in claim 1, characterized in that R_1 and R_2 are hydrogens.

6. (Amended) Derivative as defined in claim 1, characterized in that it has formula (III), where X is oxygen, one of groups R_3 and R_4 is a methyl group and the other is an α-alkene consistent with formula (II), where n+m+o equals 1 or 2 and R_1-R_2 and R_5-R_6 are hydrogens and R_9-R_{11} are methyl groups.

7. (Amended) Derivative as defined in claim 1, characterized in that it has formula (IV), where X is oxygen, R_1-R_4 are hydrogens, one of groups R_5 and R_6 is an α-alkene consistent with formula (II), where n+m+o equals 4, and R_9-R_{11} are methyl groups.

8. (Amended) Derivative as defined in claim 1, characterized in that one of groups R_9-R_{11} is an α-alkene consistent with formula (II) and two of the groups are hydrogens or C_{1-6}alkyls, and R_3-R_8 are hydrogens or C_{1-6}alkyls.

9. (Amended) Derivative as defined in claim 1, characterized in that R_{10} and R_{11} are hydrogens or C_{1-6}alkyls, R_9 is an α-alkene consistent with formula (II), where n is 0 or 1, m is 0 or 1 and o is an integer 1-4 and R_1-R_2 are hydrogens or C_{1-6}alkyls.

10. (Amended) Derivative as defined in claim 1, characterized in that it has formula (III), X is oxygen, R_1-R_4 and R_{10}-R_{11} are methyl groups, R_5-R_8 are hydrogens and R_9 is an α-alkene consistent with formula (II), where n is 0, m is 1 and o is 3.

11. (Amended) Derivative as defined in claim 1, characterized in that it has formula (III), X is oxygen, R_3-R_4 and R_{10}-R_{11} are methyl groups, R_5-R_8 are hydrogens and R_9 is an α-alkene consistent with formula (II), where m is 0 and o+n equals 1.

12. (Amended) Derivative as defined in claim 1, characterized in that one of groups R_9-R_{11} is an α-alkene consistent with formula (II) and the other groups are hydrogens or C_{1-6}alkyls, and R_3-R_8 are hydrogens or C_{1-6}alkyls or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 form a benzene ring together with the carbon atoms to which they are bonded.

13. (Amended) Derivative as defined in claim 1, characterized in that R_{10} is an α-alkene consistent with formula (II) where n is 0 or 1, m is 0 or 1 and o is an integer 1-4 and R_1 and R_2 are methyl groups, R_9 is a C_{1-6}alkyl, R_{11} is a hydrogen, R_7 and R_8 are together an oxygen atom and R_4 and R_5, together with the carbon atoms to which they are bonded, form a benzene ring.

14. (Amended) Derivative as defined in claim 1, characterized in that it is 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane, 6-hydroxy-2,5,7,8-tetramethyl-2-(prop-2-enyl)-chromane, 6-hydroxy-2,2,7,8-tetramethyl-5-(1,1-dimethyl-hex-5-enyl)-chromane, 6-hydroxy-2,2,7,8-tetramethyl-5-(prop-2-enyl)-chromane, 5-hydroxy-4,6,7-trimethyl-3-(hex-5-enyl)-benzofurane or a hydroxythioxanthone derivative.

20. (Amended) Stabilized copolymer as defined in claim 17, characterized in that the olefin is ethylene, propylene, butylene and/or pentene.

21. (Amended) Stabilized copolymer as defined in claim 17, characterized in that the aromatic compound is styrene.

22. (Amended) Stabilized copolymer as defined in claim 17, characterized in that the copolymer consists of one olefin or styrene monomer and comonomer consistent with formula (III), (IV) or (V).

23. (Amended) Stabilized copolymer as defined in claim 17, characterized in that the copolymer has a substantially regular structure.

26. (Amended) Method as defined in claim 24, characterized in that the copolymerization is performed using a metallocene catalyst or its derivative.

27. (Amended) Method as defined in claim 24, characterized in that the catalyst used in copolymerization contains a π-cyclo-pentadienyl transition metal compound and an alumoxane compound.

28. (Amended) Method as defined in claim 24, characterized in that the catalyst used in copolymerization contains a π-cyclo-pentadienyl transition metal compound and a compound containing boron.

29. (Amended) Method as defined in claim 24, characterized in that the comonomer has been complexed to the catalyst.

30. (Amended) Method as defined in claim 24, characterized in that the olefin is ethylen, propylene, butylene and/or pentene.

31. (Amended) Method as defined in claim 24, characterized in that the aromatic compound is styrene.

32. (Amended) Method as defined in claim 24, characterized in that the amount of monomer and stabilizing comonomer supplied into the process is exactly defined.

REMARKS

The present Preliminary Amendment is being filed in order to provide an Abstract of the Disclosure as new page 34 of the specification, to make of record the claim to priority and to rewrite a number of the claims to eliminate their multiple dependency and to bring these claims into the proper format for U.S. prosecution.

Applicant believes the application is in condition for examination and respectfully requests same.

Examination of this application is requested.

Respectfully submitted,

ANDRUS, SCEALES, STARKE & SAWALL, LLP

By Thomas M. Wozny

Thomas M. Wozny
Reg. No. 28,922

Andrus, Sceales, Starke & Sawall, LLP
100 East Wisconsin Avenue, Suite 1100
Milwaukee, WI 53202
(414) 271-7590
Attorney Docket No.: 2534-00066

VERSION WITH MARKINGS TO SHOW CHANGES MADE

Applicants: Markku Auer et al

Attorney Docket No. 2534-00066

IN THE SPECIFICATION:

The following heading and paragraph at page 1 have been added between the title and the first line of text as follows:

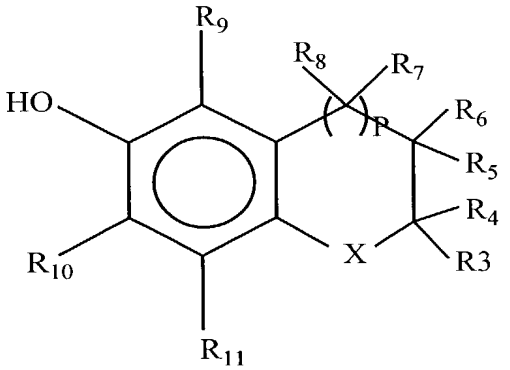
CROSS-REFERENCE TO RELATED APPLICATIONS

This application is the U.S. national stage application of International Application PCT/FI00/00585, filed June 28, 2000.

IN THE CLAIMS:

Claims 1, 4-14, 20-23, and 26-32 are amended as follows.

1. (Amended) E-vitamin derivative or a compound analogous with it, having the formula (I)



(I)

where X is an oxygen or sulfur atom, p is an integer 0 to 1, and R_3-R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II)

$$-(CH_2)_n-(CR_1R_2)_m-(CH_2)_o-CH=CH_2 \quad (II)$$

where n, m and o are integers 0-4 independent of each other and m+n+o is an integer 1-6 and R_1 and R_2 are identical or different groups selected from hydrogen or C_{1-6}alkyl or C_{1-6}alkene, which may be substituted with an aromatic ring,

or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene.

4. (Amended) Derivative as defined in claim 1 ~~or 2~~, characterized in that one of groups R_3 and R_4 or one of groups R_5 and R_6 is hydrogen or a C_{1-6}alkyl and the other an α-alkene consistent with formula (II) and R_7-R_{11} are hydrogens or C_{1-6}alkyls.

5. (Amended) Derivative as defined in ~~any one of claims 1, 2 or 4~~claim 1, characterized in that R_1 and R_2 are hydrogens.

6. (Amended) Derivative as defined in claim 1~~, 2 or 4-5~~, characterized in that it has formula (III), where X is oxygen, one of groups R_3 and R_4 is a methyl group and the other is an α-alkene consistent with formula (II), where n+m+o equals 1 or 2 and R_1-R_2 and R_5-R_6 are hydrogens and R_9-R_{11} are methyl groups.

7. (Amended) Derivative as defined in claim 1~~, 2 or 4-5~~, characterized in that it has formula (IV), where X is oxygen, R_1-R_4 are hydrogens, one of groups R_5 and R_6 is an α-alkene consistent with formula (II), where n+m+o equals 4, and R_9-R_{11} are methyl groups.

8. (Amended) Derivative as defined in claim 1 ~~or 2~~, characterized in that one of groups R_9-R_{11} is an α-alkene consistent with formula (II) and two of the groups are hydrogens or C_{1-6}alkyls, and R_3-R_8 are hydrogens or C_{1-6}alkyls.

9. (Amended) Derivative as defined in ~~any one of claims 1, 2 or 8~~claim 1, characterized in that R_{10} and R_{11} are hydrogens or C_{1-6}alkyls, R_9 is an α-alkene

consistent with formula (II), where n is 0 or 1, m is 0 or 1 and o is an integer 1-4 and R_1-R_2 are hydrogens or C_{1-6}alkyls.

10. (Amended) Derivative as defined in ~~any one of claims 1, 2 or 8-9~~claim 1, characterized in that it has formula (III), X is oxygen, R_1-R_4 and R_{10}-R_{11} are methyl groups, R_5-R_8 are hydrogens and R_9 is an α-alkene consistent with formula (II), where n is 0, m is 1 and o is 3.

11. (Amended) Derivative as defined in ~~any one of claims 1, 2 or 8-9~~claim 1, characterized in that it has formula (III), X is oxygen, R_3-R_4 and R_{10}-R_{11} are methyl groups, R_5-R_8 are hydrogens and R_9 is an α-alkene consistent with formula (II), where m is 0 and o+n equals 1.

12. (Amended) Derivative as defined in claim 1 ~~or 3~~, characterized in that one of groups R_9-R_{11} is an α-alkene consistent with formula (II) and the other groups are hydrogens or C_{1-6}alkyls, and R_3-R_8 are hydrogens or C_{1-6}alkyls or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 form a benzene ring together with the carbon atoms to which they are bonded.

13. (Amended) Derivative as defined in ~~any one of claims 1, 3 or 12~~claim 1, characterized in that R_{10} is an α-alkene consistent with formula (II) where n is 0 or 1, m is 0 or 1 and o is an integer 1-4 and R_1 and R_2 are methyl groups, R_9 is a C_{1-6}alkyl, R_{11} is a hydrogen, R_7 and R_8 are together an oxygen atom and R_4 and R_5, together with the carbon atoms to which they are bonded, form a benzene ring.

14. (Amended) Derivative as defined in ~~any one of claims 1-13~~claim 1, characterized in that it is 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane, 6-hydroxy-2,5,7,8-tetramethyl-2-(prop-2-enyl)-chromane, 6-hydroxy-2,2,7,8-tetramethyl-5-(1,1-dimethyl-hex-5-enyl)-chromane, 6-hydroxy-2,2,7,8-tetramethyl-5-(prop-2-enyl)-chromane, 5-hydroxy-4,6,7-trimethyl-3-(hex-5-enyl)-benzofurane or a hydroxythioxanthone derivative.

20. (Amended) Stabilized copolymer as defined in ~~any one of claims 17-19~~claim 17, characterized in that the olefin is ethylene, propylene, butylene and/or pentene.

21. (Amended) Stabilized copolymer as defined in ~~any one of claims 17-20~~claim 17, characterized in that the aromatic compound is styrene.

22. (Amended) Stabilized copolymer as defined in ~~any one of claims 17-21~~claim 17, characterized in that the copolymer consists of one olefin or styrene monomer and comonomer consistent with formula (III), (IV) or (V).

23. (Amended) Stabilized copolymer as defined in ~~any one of claims 17-22~~claim 17, characterized in that the copolymer has a substantially regular structure.

26. (Amended) Method as defined in claim 24~~ or 25~~, characterized in that the copolymerization is performed using a metallocene catalyst or its derivative.

27. (Amended) Method as defined in ~~any one of claims 24-26~~claim 24, characterized in that the catalyst used in copolymerization contains a π-cyclo-pentadienyl transition metal compound and an alumoxane compound.

28. (Amended) Method as defined in ~~any one of claims 24-27~~claim 24, characterized in that the catalyst used in copolymerization contains a π-cyclo-pentadienyl transition metal compound and a compound containing boron.

29. (Amended) Method as defined in ~~any one of claims 24-27~~claim 24, characterized in that the comonomer has been complexed to the catalyst.

30. (Amended) Method as defined in ~~any one of claims 24-29~~claim 24, characterized in that the olefin is ethylen, propylene, butylene and/or pentene.

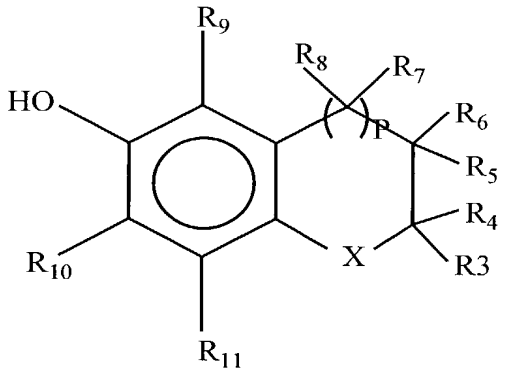
31. (Amended) Method as defined in ~~any one of claims 24-30~~claim 24, characterized in that the aromatic compound is styrene.

32. (Amended) Method as defined in ~~any one of claims 24-31~~claim 24, characterized in that the amount of monomer and stabilizing comonomer supplied into the process is exactly defined.

A COMONOMER, AND A POLYMER STABILIZED WITH IT DURING POLYMERIZATION

ABSTRACT

The invention concerns an E-vitamin derivative or a compound analogous with it, having formula (I), where X is an oxygen or sulfur atom, p is an integer 0 or 1, and R_3-R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having formula (II), where n, m and o are integers 0-4 independent of each other and R_1 and R_2 are identical or different groups selected from hydrogen or C_{1-6}alkyl or C_{1-6}alkene, which may be substituted with an aromatic ring, or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene.



(I)

$$-(CH_2)_n-(CR_1R_2)_m-(CH_2)_o-CH=CH_2 \qquad (II)$$

The invention also concerns the use of a derivative consistent with formula (I) as a stabilizing comonomer, and a stabilized copolymer and a method for the production of a stabilized copolymer.

A COMONOMER, AND A POLYMER STABILIZED WITH IT DURING POLYMERIZATION

The present invention relates to an E-vitamin derivative or a compound analogous with it as defined in the preamble of claim 1, to a method for the production of the aforesaid derivative, to its use as defined in claim 16, to a stabilized copolymer as defined in the preamble of claim 17 and to a method for the production of a stabilized copolymer as defined in the preamble of claim 24.

In prior art, specification FI 92212 presents a method for the production of a stable α-olefin polymer using a Ziegler-Natta type catalyst in which the α-olefin reacts with a complex comprising a metal of group I-IV of the periodic system and an α-alkenyl substituted stabilizer co-ordinated to it with a heteroatom as a ligand. The catalyst is attached to a magnesium carrier, and a chain of at least 5 carbons is needed between the stabilizer residue of the stabilizer ligand and the polymerizing functional unsaturated bond.

Further, specification DE 1947590 describes how a component containing a hydrocarbon based, sterically protected hydroxyl group and linked to an α-vinyl group situated at a distance of at least two carbon atoms is copolymerized in the polymerization conditions of olefins in the presence of an old-generation Ziegler-Natta catalyst. The problem is a low polymerization activity.

A generally known practice is to polymerize polyolefins using Ziegler-Natta type catalysts. The catalyst consists of a metalorganic compound in which the procatalyst is typically an at least partially reduced compound of a transition metal of group IV, V, VI or VII, usually a compound of e.g. titan or zirconium, while the cocatalyst is an organometallic compound of an alkali metal, alkaline earth metal, zinc

or aluminum, e.g. triethylaluminum and diethylmagnesium. An example of such a catalyst is a combination of titan chloride and triethylaluminum. The activity increases considerably when the above-mentioned components are attached to a fixed carrier; e.g. $MgCl_2$. Ziegler-Natta catalysts are characterized by an ability to give the polymer the particle form of the catalyst during polymerization, thus producing polymer particles of 0.2 - 5 mm. The polymer particle thus produced is porous, and without an additive increasing the stability, it is chemically dissolved during use.

A known practice is to use a stabilizer having a large molar mass, e.g. derivatives of tert-butyl phenol and pentaerythritol, as an additive. Another known practice is to use polymer-based and oligomeric molecules. A limitation is, however, a lower solubility in polymer. Substituted phenols and aromatic amines are widely used antioxidants. Usually the polymer product obtained after the polymerization reaction is melted in a so-called extruder stage, and additives improving stability are added to the molten product, whereupon the product is granulated.

Further, the use of so-called metallocene catalysts is known in industry. Such catalysts have been used since the early 1990's in polymerization processes beside or instead of Ziegler-Natta catalysts. Metallocene catalysts are based on a so-called sandwich structure, in which a metallic center, e.g. zirconium, is placed between two cyclopentadienyl rings (bischloro-zirconocene), and on derivatives of that structure. Metallocene catalysts have in some cases increased the polymerization activity even with comonomers that have previously been difficult to copolymerize. Therefore, metallocenes are increasingly used in various industrial applications.

A problem with previously known methods is that the stabilizing additive is added to the product

at the extruder stage, which is why it has not been possible to utilize a catalyst producing a particle product and a polymerization process because of the stability problem.

A further problem is that the additives in the polymer product vanish during use. One of the reasons for this is that the additives improving stability drift to the surface of the product, with the result that the stabilizing effect is diminished and disappears with time and that the additives may get into contact e.g. with foodstuffs. In addition, it has been established that some additives have estrogenic effects. The loss of additives in the product may also be partly due to evaporation taking place during processing or dissolution occurring during washing.

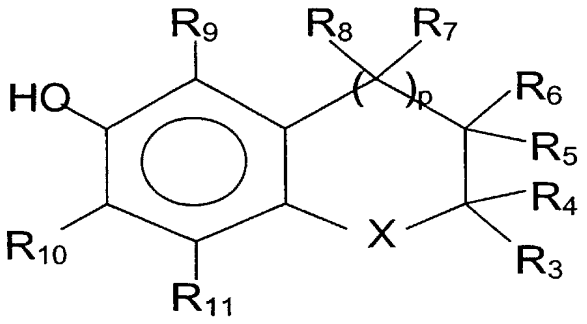
Another problem is irregular distribution of additives in the polymer product. Irregular distribution may result e.g. from an incompatibility of the stabilizers with paraffin-type hydrocarbon-based polymers due to a high polarity. In addition, the amount of stabilizer added to polyolefins has to be limited because of the tendency of the stabilizers to crystallize.

Further problems are a poor product yield and an atacticity of the product in polymerization carried out using a Ziegler-Natta catalyst.

The object of the invention is to eliminate the problems referred to above and to disclose a new usable comonomer having a stabilizing effect. A further object of the invention is to disclose a copolymer stabilized during polymerization.

The E-vitamin derivative or the compound analogous with it, its production method and the stabilized copolymer and its production method according to the invention are characterized by what is presented in the claims.

The E-vitamin derivative of the invention or the compound analogous with it, i.e. a compound having a corresponding structure, has the following formula (I):



(I)

where X is an oxygen or sulfur atom, p is an integer = 0 or 1, and R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II)

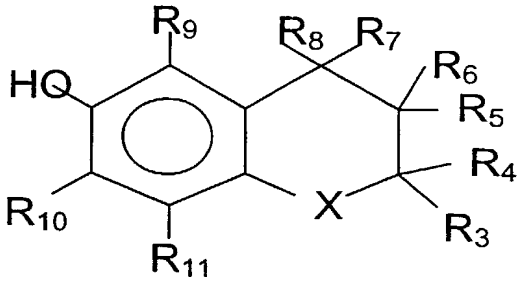
$$-(CH_2)_n-(CR_1R_2)_m-(CH_2)_o-CH=CH_2 \qquad (II)$$

where n, m and o are integers 0 - 4 independent of each other and R_1 and R_2 are identical or different groups selected from hydrogen or C_{1-6}alkyl or C_{1-6}alkene, which may be substituted with an aromatic ring, e.g. a styrene derivative

or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene.

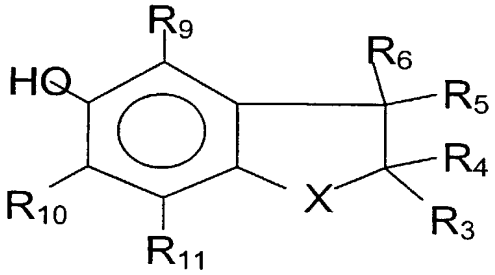
C_{1-6}alkyl or C_{1-6}alkene means a branched or non-branched hydrocarbon chain containing 1 - 6 carbon atoms.

In an embodiment of the invention, the derivative has the formula (III)



(III)

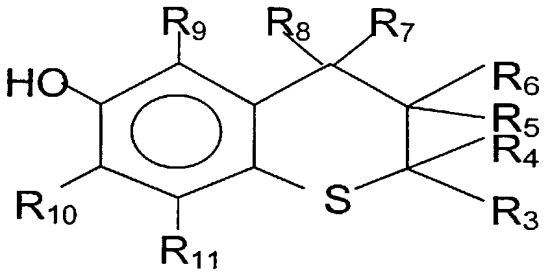
or the formula (IV)



(IV)

where X is an oxygen or sulfur atom and R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II).

In an embodiment of the invention, the derivative has the formula (V)



(V)

where R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II),

or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene

ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene.

The E-vitamin derivative of the invention or the compound analogous with it preferably has a structure containing at least one fused benzene ring and a ring containing a heteroatom, and an α-chain linked with them. The heteroatom, such as an oxygen or sulfur atom, and the hydroxy group are preferably bonded to opposite sides of the benzene ring of the heterocycle, with the result that an effect stabilizing the compound is produced.

One group of E-vitamin derivatives according to the invention is formed by compounds consistent with formula (III) or (IV), where one the 2-position groups R_3 and R_4 or 3-position groups R_5 and R_6 is hydrogen or C_{1-6}alkyl and the other an α-alkene consistent with formula (II), R_7 - R_{11} are hydrogens or C_{1-6}alkyls and the sum of integers m, n and o is 1 - 12 and R_1 and R_2 are as specified above.

A preferred group of compounds according to the invention are compounds (III) or (IV) in which one of the heterocycle 2-position groups R_3 and R_4 or of the heterocycle 3-position groups R_5 and R_6 is a hydrogen or C_{1-6}alkyl while the other is an α-alkene consistent with formula (II), where n + m + o is an integer 1 - 6 and R_1 and R_2 are hydrogens and R_9 - R_{11} are C_{1-6}alkyls. In an embodiment, the derivative is a compound consistent with formula (III), where X is oxygen, one of groups R_3 and R_4 is a methyl group and the other is an α-alkene consistent with formula (II), where n + m + o equals 1 or 2 and R_1 and R_2 are hydrogens, R_5 - R_8 are hydrogens and R_9 - R_{11} are methyls. R_3 or R_4 may alternatively be a hydrogen instead of a methyl group. In an embodiment, the derivative is a compound consistent with formula (IV), where X is oxygen, R_1 - R_4 are hydrogens, one of groups R_5 and R_6 is

an α-alkene consistent with formula (II), where n + m + o equals 4, and R_9 - R_{11} are methyl groups.

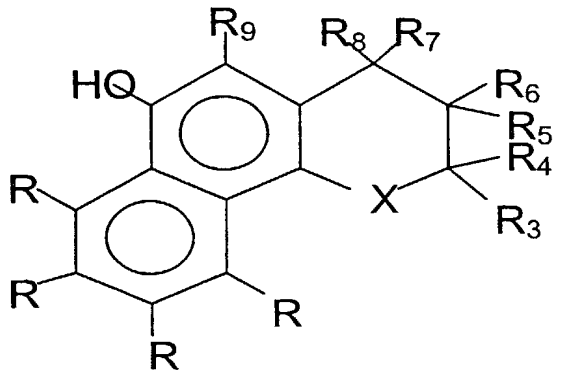
Another group of E-vitamin derivatives according to the invention consists of compounds consistent with formula (III) or (IV) where one of groups R_9 - R_{11} in 5, 7 and 8-position (formula III) or 4, 6 and 7-position (formula IV) in the heterocycle is an α-alkene consistent with formula (II) and two of the groups are hydrogens or C_{1-6}alkyls, and the sum of the integers m, n and o is in the range of 1 - 12 and R_1 and R_2 are as specified above.

A preferred group of compounds according to the invention consists of compounds (III) or (IV) in which R_9 in 5-position (formula III) or 4-position in the heterocycle is an α-alkene consistent with formula (II) where the integer n is 0 or 1, m is 0 or 1 and o is 1 - 4 and R_1 and R_2 are hydrogens or C_{1-6}alkyls. R_{10} and R_{11} are hydrogens or C_{1-6}alkyls. In a preferred case, in a derivative consistent with formula (III), X is oxygen, R_1 - R_4 and R_{10} - R_{11} are methyls, R_5 - R_8 are hydrogens and R_9 is an α-alkene consistent with formula (II) where n is 0, m is 1 and o is 3. In an embodiment, the derivative is a compound consistent with formula (III) where X is oxygen, R_3 - R_4 and R_{10} - R_{11} are methyl groups, R_5 - R_8 are hydrogens and R_9 is an α-alkene consistent with formula (II) where m is 0 and n + o is 1.

E-vitamin derivatives consistent with formula (III) include e.g. 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane, 6-hydroxy-2,5,7,8-tetramethyl-2-(prop-2-enyl)-chromane, 6-hydroxy-2,2,7,8-tetramethyl-5-(1,1-dimethyl-hex-5-enyl)-chromane and 6-hydroxy-2,2,7,8-tetramethyl-5-(prop-2-enyl)-chromane. E-vitamin derivatives consistent with formula (IV) include e.g. 5-hydroxy-4,6,7-trimethyl-3-(hex-5-enyl)-benzofurane.

In an embodiment of the invention, the compound analogous with the E-vitamin derivative is a compound consistent with formula (IV) in which one of groups R_9 - R_{11} is an α-alkene consistent with formula (II) and the other groups are hydrogens or C_{1-6}alkyls and R_3 - R_8 are hydrogens or C_{1-6}alkyls. Alternatively, R_7 and R_8 are together an oxygen atom and/or R_4 and R_5, together with the carbon atoms to which they are bonded, form a benzene ring. In a preferred embodiment, R_{10} is an α-alkene consistent with formula (II) where n is 0 or 1, m is 0 or 1 and o is an integer 1 - 4 and R_1 and R_2 are methyl groups, R_9 is a C_{1-6}alkyl, R_{11} is a hydrogen, R_7 and R_8 are together an oxygen atom and R_4 and R_5, together with the carbon atoms to which they are bonded, form a benzene ring. A compound consistent with formula (V) may be e.g. a thioxanthone derivative, such as a hydroxythioxanthone derivative.

The derivative according to the invention may naturally have any kind of structure corresponding to those described above, e.g.



An E-vitamin derivative consistent with formula (I) or a compound analogous with it is produced using suitable synthesizing methods of organic chemistry.

The E-vitamin derivative of the invention or the compound (I) analogous with it can be produced e.g.

A) by allowing a hydroquinone derivative to react with a suitable tertiary unsaturated alcohol or thiol.

In method A), a compound consistent with formula (I) can be produced directly by allowing a hydroquinone derivative, such as a mono-, di- or trialkyl-hydroquinone, e.g. dimethyl or trimethyl hydroquinone, to react with a suitable unsaturated alcohol, such as alka-dienol, e.g. 2,7-octadien-1-ol or 3-methyl-1,6-heptadien-3-ol, or thiol in a suitable solvent. Optionally, according to method A), in a first stage it is possible to prepare an intermediate product containing a (halogen-alkyl) group or a corresponding group by allowing a hydroquinone derivative to react with a suitable unsaturated alcohol, such as 2-alkyl-alka-1,x-dien-3-ol, e.g. 3-methylhept-1,6-dien-3-ol or 3-alkyl-x-halogen-alk-1-en-3-ol, e.g. 3-methyl-5-chlor-pent-1-en-3-ol, or thiol in the presence of a suitable catalyst in a suitable solvent. In a second stage, a compound consistent with formula (I) is prepared by splitting off a hydrogen halogenide or a corresponding compound from the halogen alkyl group or an equivalent group in the intermediate product in the presence of an alkali. A suitable catalyst is e.g. a metal halide, such as aluminum chloride and zinc chloride. Suitable solvents are e.g. acids, such as formic acid, sulfuric acid or equivalent, tetrahydrofurane (THF) and dichloromethane. A suitable alkali is e.g. 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU).

An E-vitamin derivative or a compound (I) analogous with it as provided by the invention can be produced e.g.

B) by allowing a hydroquinone derivative to react with a suitable unsaturated alcohol or thiol and

adding an α-alkene to the fused heterocyclic derivative thus formed.

In a first step in method B), a fused heterocyclic derivative can be produced by allowing a hydroquinone derivative, such as mono-, di- or trialkylhydroquinone, to react with a suitable tertiary unsaturated alcohol, such as 3-alkyl-alk-1-en-3-ol e.g. 3-methyl-but-1-en-3-ol or thiol, in the presence of a suitable catalyst in a suitable solvent. A suitable catalyst is e.g. a metallic halide, such as aluminum chloride and zinc chloride. Suitable solvents are e.g. tetrahydrofurane (THF) and dichloromethane and acids, e.g. formic acid. In a second step in the method, an α-alkene consistent with formula (II) is added to the heterocyclic derivative in acid conditions.

The E-vitamin derivative of the invention or a compound analogous with it is preferably used as a stabilizing comonomer, i.e. as a stabilizer, in copolymerization to produce a stabilized copolymer. The function of the stabilizer is to prevent and reduce the harmful effects of heat, UV radiation, oxygen and/or ozone on the copolymer.

The stabilized copolymer consists of at least one monomer variety and a stabilizing comonomer. The monomer in question is an olefin and/or a cyclic and/or aromatic compound containing an α-alkene chain. The olefin monomer may be e.g. ethylene, propylene, 1-butene, isobutene and/or 4-methyl-1-pentene or the like or a mixture of these. The aromatic compound may be styrene. Naturally, the monomer may be of any type. The stabilizing comonomer is an E-vitamin derivative or a compound analogous with it which has the formula (I) and which has a clearly stabilizing effect and which can be polymerized under normal polymerization conditions. The stabilizing comonomer may be e.g. a derivative of chromane-, benzofurane- or hydroxythioxanthone.

The comonomer, i.e. stabilizer of the invention, is preferably bonded by its α-alkene chain to a copolymer.

In an embodiment of the invention, the copolymer comprises one olefin or styrene monomer variety and an E-vitamin derivative according to the invention or a compound analogous with it having the formula (III), (IV) or (V).

The copolymer preferably belongs to so-called addition polymers. When an addition polymer is formed, no small-molecule side products are generated, i.e. the structural unit of the polymer has a monomeric composition. Monomers may have a linear or a branched hydrocarbon chain, and they contain at least one dual bond enabling a polymerization reaction to take place.

In the copolymer, different monomer varieties may be arranged in different ways, e.g. in a regular fashion, such as alternately, as a segment or in other ways like this. The monomers may also be arranged in an irregular fashion. The structure of the copolymer is preferably mainly regular, such as isotactic or syndiotactic, as is typically the case when monomers are polymerized using metallocene or Ziegler-Natta catalysts (stereospecific polymerization). A feature characteristic of especially products obtained via polymerization using metallocene catalysts is a syndiotactic form. The crystallizing properties of the polymer depend on the regularity of the structure, among other things. However, the polymer may also contain atactic parts or it may completely atactic.

In the method of the invention for the production of a stabilized copolymer, at least one monomer variety and a stabilizing comonomer are copolymerized in the presence of a catalyst in a single-stage or multi-stage polymerization process known in itself, using e.g. precipitation, solution or gas phase polymerization, which will not be described here in detail.

According to an embodiment, the catalyst used in copolymerization is preferably e.g. a liquid or solid metallocene catalyst or its derivative known in itself, which is formed from derivatives of transition metals, including lanthanides. Among the best transition metals for the production of catalysts are transition metals belonging to groups 3 and 4, and lanthanides whose oxidation number is +2, +3 or +4. The metallocene components contain 1 - 3 anionic or neutral groups having a π-bond. To improve the activity of the catalyst, a cocatalyst, which often consists of methylalumoxane (MAO), is generally used. More preferably, MAO can be replaced e.g. with compounds containing boron, e.g. tri(hydrocarbyl)boron and its halogenated derivatives. The cocatalyst used may be e.g. tetraphenyl borate. In the copolymerization method of the invention, it is possible to use e.g. a metallocene catalyst of the type described in patent application FI 941662. Naturally, in the copolymerization method in question, it is also possible to use other catalysts used in this field. The catalyst may comprise a solid carrier. The carrier may consist of any carrier material, which will not be described here in detail.

In an embodiment of the invention, the catalyst used in copolymerization contains a π-cyclopentadienyl transition metal compound and an alumoxane compound. In an alternative embodiment, the catalyst contains a π-cyclo-pentadienyl transition metal compound and a compound containing boron.

In an embodiment, the stabilizing comonomer is chemically complexed e.g. by its heteroatom to the catalyst, being bound via a chemical bond e.g. to a Zr atom of the catalyst. The comonomer may naturally also be used as such or mixed with other monomers e.g. in the polymerization solution during polymerization.

At the polymerization stage, the stabilizing comonomer and the monomers, e.g. olefin and/or styrene monomers, are copolymerized, in which process the comonomer of the invention is polymerized substantially along with other monomers, being simultaneously chemically bound to the copolymer. The monomer to be polymerized is bound to an active point, e.g. a Zr atom in the catalyst, causing faster polymerization. The polymer grows as the structural units of the copolymer are increasing. The copolymer contains different monomers in certain proportions.

The copolymer may be e.g. an ethylene/-, propylene/-, butylene/- or styrene/E-vitamin derivative-copolymer. The copolymerization product may naturally consist of more than two monomer varieties. Using different production methods and proportions of different monomers, it is possible to adjust the properties of the copolymer.

Copolymers as provided by the invention can be used either as such or in a mixture with other polymers. A copolymer stabilized with a comonomer according to the invention can be used e.g. as packing material in the foodstuff industry.

The E-vitamin derivative of the invention or the compound analogous with it has the advantage that it is able to polymerize in typical polymerization conditions with a good yield and that it has a good ability to inhibit oxidation, allowing it to be used as an oxidation inhibitor in polymer production. Furthermore, the comonomer improves the adhesion properties of polymers e.g. with respect to fillers.

The copolymer of the invention has the advantage that the stabilizing comonomer, i.e. stabilizer, is chemically bonded to the polymer structure during polymerization, which means that it is uniformly distributed in the entire polymer and the chemical bonds prevent the loss of stabilizer in the product, in

other words, they prevent the stabilizer from drifting toward the surface of the product during use. Thus, the stabilizer will not drift e.g. to a foodstuff protected with plastic and is therefore not transferred to people.

The copolymerization method of the invention has the advantage that it allows the use of a metallocene catalyst. In polymerization conditions, such a catalyst works better than other catalysts known at present. When the metallocene catalyst in question is used, a polymer product having a syndiotactic structure and therefore a higher melting point can be manufactured.

A further advantage provided by copolymerization according to the invention is that stabilization is performed during polymerization, in other words, the stabilizer is added as a comonomer to the polymerization product essentially during polymerization, so that the product is directly ready for further processing, in other words, the product thus obtained need not be melted again and fed into an extruder. Thus, a saving is also made in the investment costs of the extruder, which may amount to several tens of millions, even over a hundred million FIM.

In the following, the invention will be described by the aid of a detailed examples of its embodiments with reference to the drawings, wherein

Fig. 1 presents the results of a mass spectrometry analysis of a comonomer according to the invention, 5-hydroxy-4,6,7-trimethyl-3-(hex-5-enyl)-benzofurane,

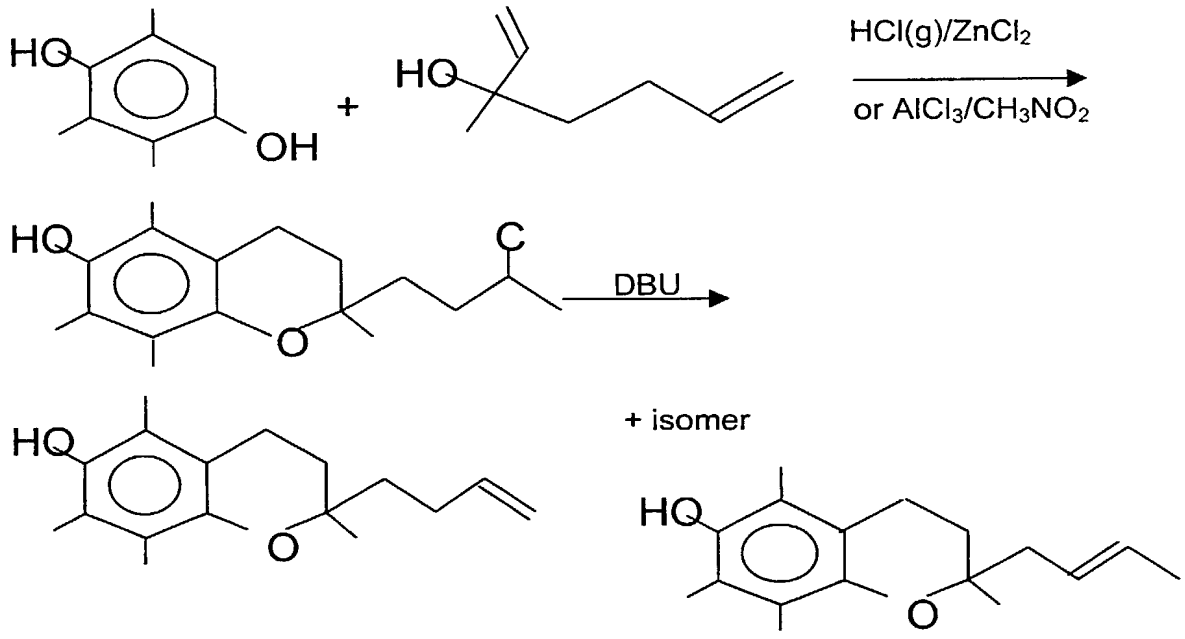
Fig. 2 presents the results of an NMR-spectrometry analysis of a comonomer according to the invention, 5-hydroxy-4,6,7-trimethyl-3-(hex-5-enyl)-benzofurane,

Fig. 3 presents the results of a mass spectrometry analysis of a comonomer according to the in-

vention, 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane, and

Fig. 4 presents the results of an NMR-spectrometry analysis of a comonomer according to the invention, 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane.

Example 1; preparation of 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane.



Preparation of 3-methylhept-1,6-dien-3-ol:

To 232 g (0.4 mol) of vinyl magnesium chloride in THF was added a solution consisting of 35 g (0.36 mol) of 5-hexene-2-one in 150 ml of anhydrous THF. The reaction mixture was stirred for 20 h at room temperature, whereupon it was cautiously poured into 450 ml of cold, saturated, aqueous NH_4CL solution. The organic extract was concentrated and diffused with dichloromethane, dried using Na_2SO_4 and concentrated. The residue was distilled, and the yield obtained was 35.5 g (78%) 3-methylhept-1,6-dien-3-ol; t.p. 45 °C/10 mmHg.

Preparation of 6-hydroxy-2,5,7,8-tetramethyl-2-(4-chloro-butyl)-chromane:

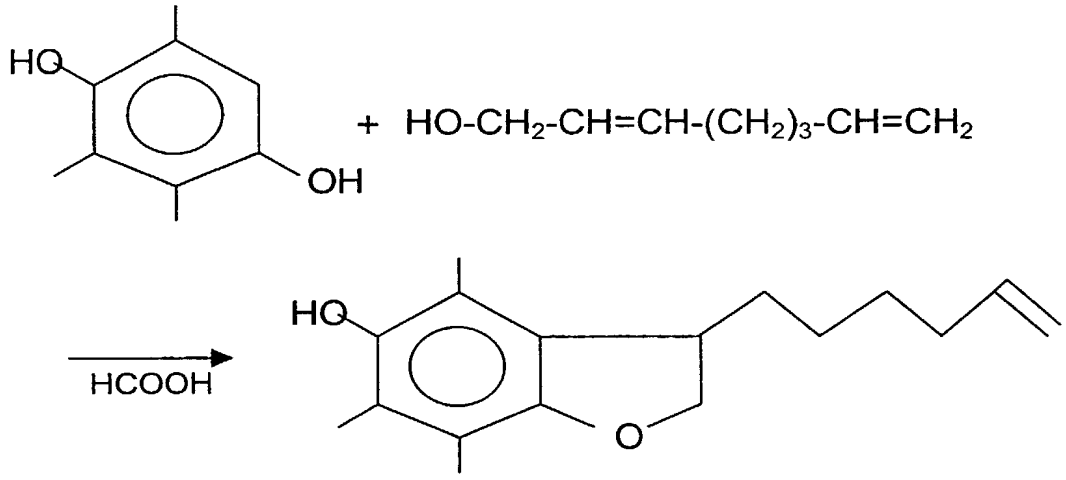
A suspension containing 20 g (0.150 mol) anhydrous $AlCl_3$ in 200 ml of dichloromethane was stirred at 0 °C while at the same time adding 25.8 g (0.42 mol) of CH_3NO_2 under a protective layer of argon. After the mixture had been stirred for 10 min at 0°C, 30.4 g (0.2 mol) of trimethyl-hydroquinone was added in batches. The brown suspension obtained as a result was cooled to -20 °C and a solution consisting of 3-methylhept-1,6-dien-3-ol in 750 ml of dichloromethane was added drop by drop during 0.5 h. The mixture thus produced was allowed to cool down slowly to room temperature, and it was stirred overnight, whereupon it was poured on ice/water. The organic layer was collected, washed twice using a $NaHCO_3$ solution and concentrated. The yield thus obtained was 40 g of a raw product containing insignificant impurities. The raw product was distilled, and the yield thus produced was 15 g (25 %) of 6-hydroxy-2,5,7,8-tetramethyl-2-(4-chlorobutyl)-chromane fraction in the form of a light brown liquid, t.p. 180 °C/1 mmHg, which was crystallized overnight in a cooler mp X °C. ^1H NMR: 1.22 (s, 3H, CH_3-C(2)); 1.5(d, 3H, -$CHClCH_3$) 1.65 (m, 2H, $ArCH_2$-CH_2-) 1.8 (m, 4H, -CH_2-CH_2-) 2.1, 2.12, 2.15 (3S, 9H, $ArCH_3$); 2.62 (t, 2H, CH_2Ar); 4.1 (m, 1H, CH) and 4.23 (s, 1H, OH). ^{13}C NMR: 11.3, 11.8, 12.2, 20.7, 23.6, 25.2, 31.3, 34.4, 36.7, 59.1, 73.9, 117.1, 118.5, 121.1, 122.5, 144.7 and 145.2.

Preparation of 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane:

To 14.8 g (0.05 mol) of 6-hydroxy-2,5,7,8-tetramethyl-2-(4-chlorobutyl)-chromane was added 36.3 g (0.24 mol) of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) and the solution was heated to 120 °C and stirred for 20 h. After that, the reaction mixture was

allowed to cool down to room temperature, poured into 350 ml of dichloromethane and washed repeatedly using diluted HCl. The organic layer was concentrated, and the yield thus obtained was 10.2 g of raw product that was free of DBU. In addition, the material was purified by distilling, and the result thus obtained was 5g (38 %) of 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane; t.p. 154 °C/1mmHg.

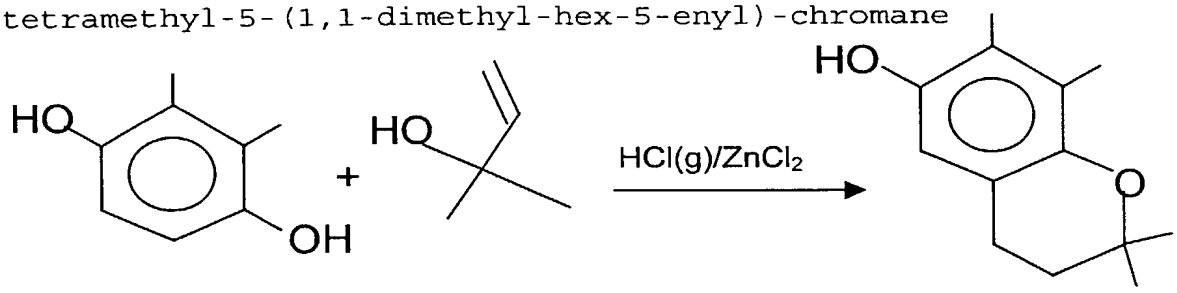
Example 2; preparation of 5-hydroxy-4,6,7-trimethyl-3-(hex-5-enyl)-benzofurane:

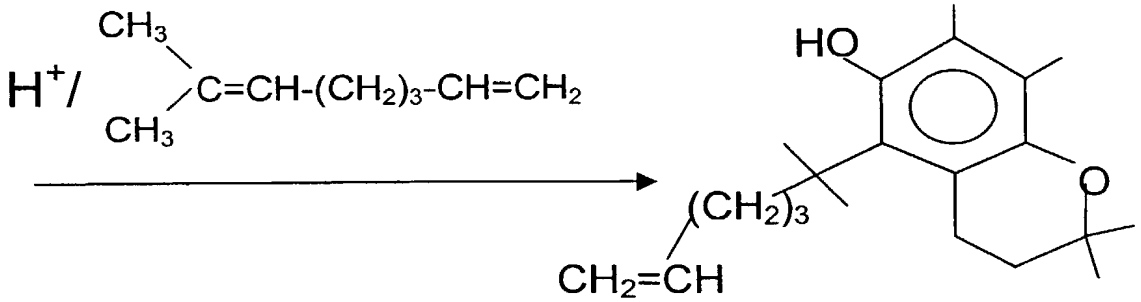


Trimethyl hydroquinone (23.7 g) and 2,7-octadien-1-ol (19.7 g) were weighed and put into a reaction vessel and 50 ml of formic acid was added into the mixture. The temperature of the mixture was raised to the boiling point of formic acid, and the reaction was allowed to continue for three hours. The reaction mixture was poured into 150 ml of ice-water mixture, and the organic phase was recovered in diethyl ether. The organic solvent was evaporated, whereupon 100 ml of methanol and 1 ml of hydrochloric acid was added to the residue. The reaction mixture was hydrolyzed at the boiling point of methanol for 30 min, whereupon the solvent was evaporated from the mixture. The mix-

ture was dissolved in diethyl ether, and the organic phase was washed twice using sodium hydrogen carbonate and five times using distilled water. The diethyl ether was evaporated. At this point, the yield was 48.0 g. n-hexane was added to the mixture, which was then stirred for 30 min at the boiling point of hexane, whereupon the mixture was allowed to cool down to room temperature. The portion not dissolved in hexane, mainly consisting of inert trimethyl hydroquinone and the product, was separated from the mixture by filtering. The solid portion was dissolved in a small amount of ethanol and precipitated by adding some water into the solution, whereupon the product (7.5 g) was separated by filtering. After that, based on mass spectrometry (Fig. 1) and NMR spectrometry (Fig. 2) analyses, the product was identified as 5-hydroxy-4,6,7-trimethyl-3-(hex-5-enyl)-benzofurane.

Example 3; preparation of 6-hydroxy-2,2,7,8-tetramethyl-5-(1,1-dimethyl-hex-5-enyl)-chromane



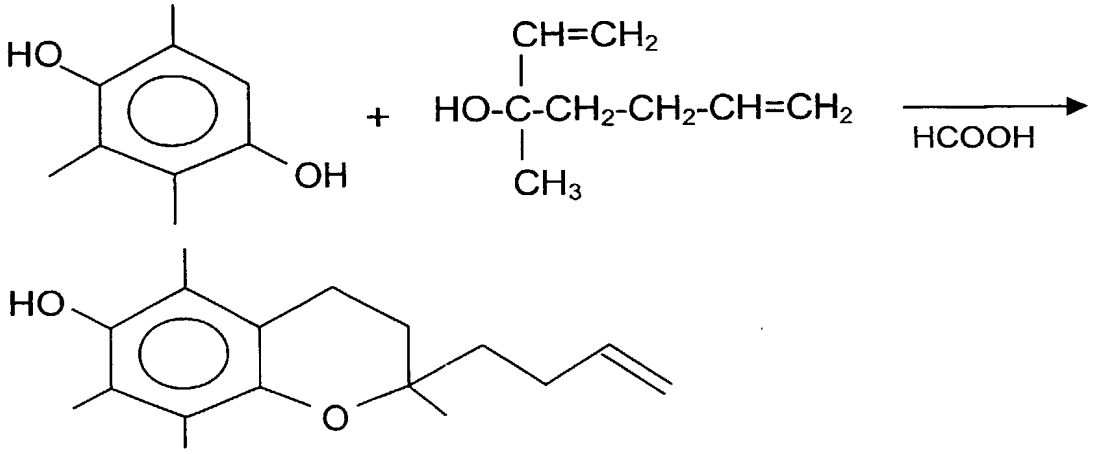


Dimethyl hydroquinone and formic acid were mixed together, and 3-methylbuten-3-ol was added little by little into the reaction mixture during one

hour. The mixture was allowed to react for 2 h at the boiling point of formic acid, whereupon the reaction was interrupted by adding some ice-water mixture into it. The organic phase was recovered in diethyl ether and washed several times with water. The organic phase was evaporated, and 75 ml of methanol and 1 ml of concentrated hydrochloric acid was added into the residue, whereupon the mixture has hydrolyzed for half an hour at the boiling point of methanol. The methanol was evaporated, and the residue was dissolved in diethyl ether, which was washed alternately twice with sodium hydrogen carbonate and five times with water. The diethyl ether was evaporated and the residue was distilled in a vacuum. The intermediate product (1.25 g), 6-hydroxy-2,2,7,8-tetramethyl-chromane, was recovered in conditions as follows: p = 0.2 mbar and T = 110 - 120 °C.

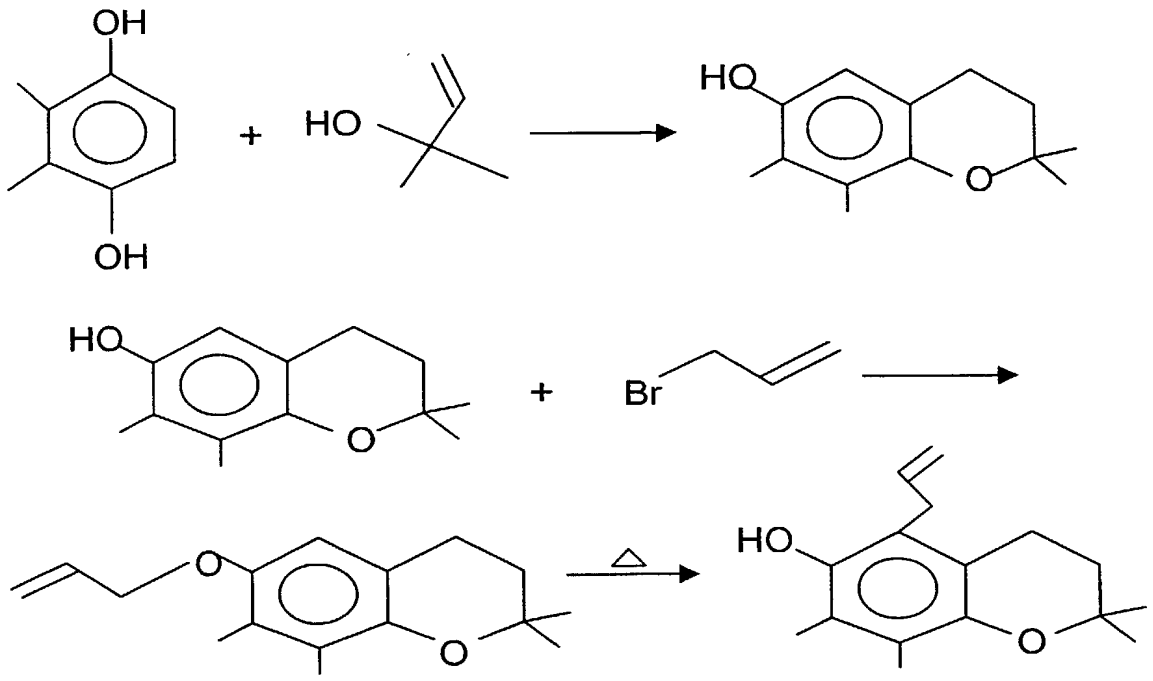
6-hydroxy-2,2,7,8-tetramethylchromane and 7-methyl-1,6-octadiene were mixed together. The reaction solution was heated, whereupon an acid catalyzer was added into it. The mixture was allowed to react during 24 hours, and the product, 6-hydroxy-2,2,7,8-tetramethyl-5-(1,1-dimethyl-hex-5-enyl)-chromane, was separated by the conventional method and purified by distilling.

Example 4; preparation of 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane



1.02 g of trimethyl hydroquinone, 0.844 g of 3-hydroxy-3-methyl-1,6-heptadiene and 10 ml of formic acid (98 %) were added into a 50-ml reaction vessel. The temperature was increased to the boiling point of formic acid, at which temperature the reaction was allowed to continue for 2 h 50 min. The reaction was interrupted by pouring the mixture into an ice-water mixture, whereupon the organic phase was recovered and washed in the conventional manner. From the product were first separated the portions not dissolved in hexane, whereupon the product was dissolved in ethanol, precipitated with water and washed using hexane and diethyl ether. The yield was 1.3 g. The product was identified via mass spectrometry (Fig. 3) and NMR spectrometry (Fig. 4) analyses as 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane.

Example 5; preparation of 6-hydroxy-2,2,7,8-tetramethyl-5-(prop-2-enyl)-chromane

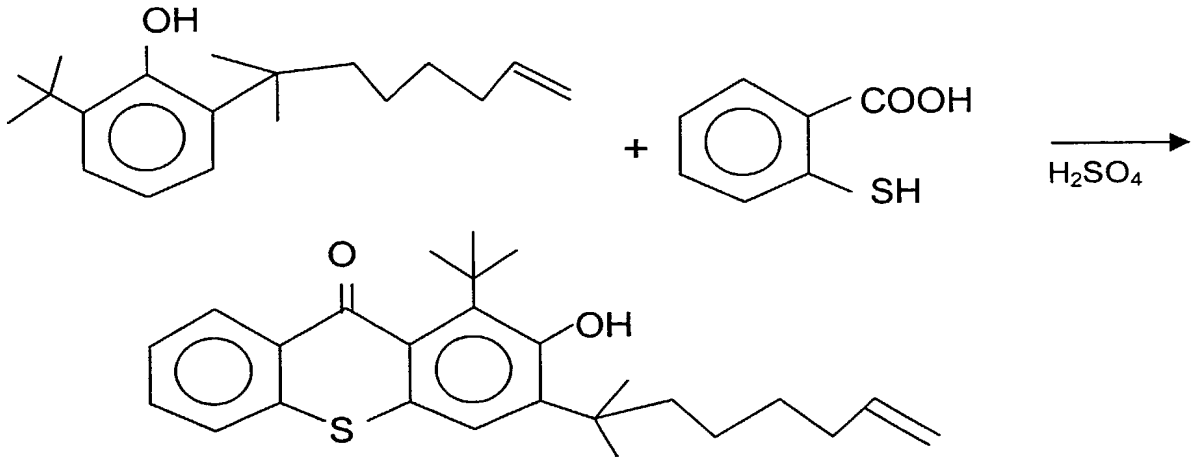


Dimethyl hydroquinone and formic acid were mixed together, and 3-methylbuten-3-ol was added little by little into the reaction mixture during one hour. The mixture was allowed to react for 2 h at the boiling point of formic acid, whereupon the reaction was interrupted by adding some ice-water mixture into the mixture. The organic phase was recovered in diethyl ether and washed several times with water. The organic phase was evaporated and 75 ml of methanol and 1 ml of concentrated hydrochloric acid was added into the residue, whereupon the mixture was hydrolyzed for half an hour at the boiling point of methanol. The methanol was evaporated, and the residue was dissolved in diethyl ether, which was washed alternately twice with sodium hydrogen carbonate and five times with water. The diethyl ether was evaporated, and the residue was distilled in vacuum. The intermediate product

(1.25 g), 6-hydroxy-2,2,7,8-tetramethyl-chromane, was recovered under the following conditions: p = 0.2 mbar and T = 110 - 120 °C.

The intermediate product (0.5 g) was dissolved in 10 ml of acetone. K_2CO_3 (0.37 g) was added gradually and the mixture was stirred for 30 min, whereupon C_3H_5Br (0.33 g) was added gradually. A reflux condenser was used during the reaction. The final product, 6-hydroxy-2,2,7,8-tetramethyl-5-(prop-2-enyl)-chromane, was obtained by heating the mixture for 48 h. The product was separated from the mixture via column chromatography.

Example 6; Preparation of hydroxythioxanthone



A hydroxythioxanthone derivative was prepared from 6-tert-butyl-(2-(1,1-dimethylhept-6-enyl))-phenol, which can be produced e.g. by a method according to patent PCT/FI95/00196, and from thiosalicylic acid in a manner known in itself.

Example 7; copolymerization

A polymerization test was carried out to experiment on copolymerization of 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane and propylene in the presence of a metallocene catalyst. The metallocene catalyst consisted of π-cyclo-pentadienyl transition metal and alumoxane.

The treatment of the π-cyclo-pentadienyl transition metal and alumoxane as well as the comonomer was performed in a nitrogen cabinet containing under 2 ppm oxygen and under 5 ppm water. The polymerization was carried out in an autoclave equipped with a turbine mixer. The reaction temperature was adjusted with an accuracy of 0.3 °C.

The dry autoclave was evacuated and rinsed with water. This was repeated three times. A first batch of distilled toluene was fed into the reactor by using nitrogen over-pressure. 5 mg of *ansa* metallocene catalyst was dissolved in a second batch of MAO/toluene solution and pre-activated by letting them interact with each other at room temperature for 5 min.

The catalyst/activator mixture was fed into the reactor. Pre-polymerization was started by adding a propylene monomer. After 3 min., a comonomer diluted with toluene was added using propylene gas, until the partial pressure of propylene reached 2 bar. The polymerization activity was monitored by measuring the propylene consumption while maintaining a constant total pressure in the reactor by continuously adding gaseous propylene. After 30 min, polymerization was interrupted by stopping the supply of propylene and adding 100 ml of methanol. Polyolefin was filtered and the catalyst residue was removed by treating the product, i.e. the copolymer, with a 1-% methanol/HCl solution. The product was washed twice with ethanol, dried in vacuum at a temperature of 50 °C and weighed. The amount of copolymer obtained was 3 g. The copolymer

was diffused using a Soxhlet device before determining the concentration of bonded stabilizer. The results of the polymerization this means that are presented in Table 1.

Table 1 shows that the OIT temperature rises as the comonomer content increases, which is an indication of the effect of the stabilizer. Further, it can be seen from Table 1 that crystallization of the product decreases at higher copolymer content levels, indicating that the comonomer is chemically bonded to the rest of the polymer.

Table 1. The results of copolymerization of 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane and propylene.

Test	Stabilizer	Zr µmol/l	Al mmol/l	Stab /Zr Mol/ Mol	Stab/ Al Mol/ mol	T_M °C	Crys %	Product kg/mol Zr h atm	OIT
1	-	42	126	-	-	128.4	73.4	5644	210
2	+	44	132	120	0.040	129.1	69.7	3984	229
3	+	44	132	120	0.040	131.0	64.6	3590	230
4	+	44	132	265	0.086	127.2	56.0	2510	244
5	+	44	132	356	0.120	129.0	58.2	2943	248

The E-vitamin derivative of the invention or the compound analogous with it is suited for use in different applications, e.g. for the manufacture of any kind of copolymer. Moreover, the copolymer of the invention is suited for use as different applications for any purpose.

The embodiments of the invention are not restricted to the examples presented above; instead, they may be varied in the scope of the following claims.

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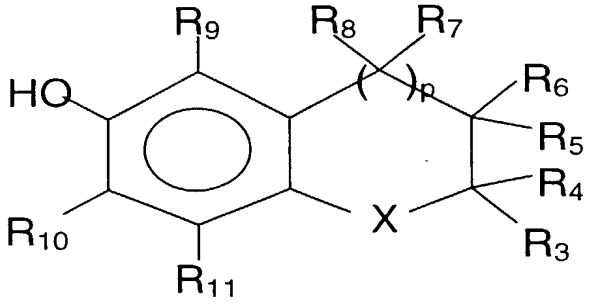
AMENDED CLAIMS

1. E-vitamin derivative or a compound analogous with it, having the formula (I)



(Ia)

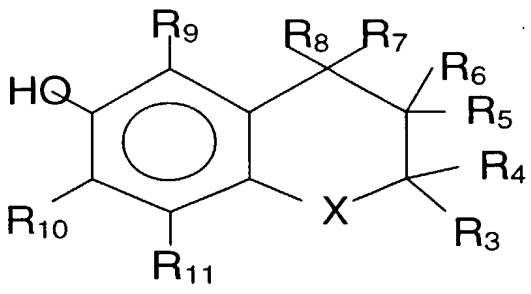
where X is an oxygen or sulfur atom, p is an integer 0 or 1, and R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II)

$$-(CH_2)_n-(CR_1R_2)_m-(CH_2)_o-CH=CH_2 \qquad (II)$$

where n, m and o are integers 0 - 4 independent of each other and m + n + o is an integer 1 - 6, and R_1 and R_2 are identical or different groups selected from hydrogen or C_{1-6}alkyl or C_{1-6}alkene, which may be substituted with an aromatic ring,

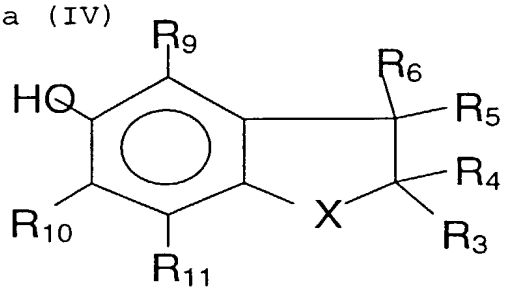
or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene.

2. Derivative as defined in claim 1, c h a r a c t e r i z e d in that it has the formula (III)



(III)

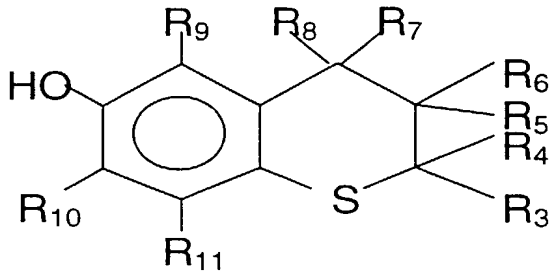
or the formula (IV)



(IV)

where X is an oxygen or sulfur atom and R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II).

3. Derivative as defined in claim 1, characterized in that it has the formula (V)



(V)

where R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II),

or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene.

4. Derivative as defined in claim 1 or 2, characterized in that one of groups R_3 and R_4 or one of groups R_5 and R_6 is hydrogen or a C_{1-6}alkyle and the other an α-alkene consistent with formula (II) and R_7 - R_{11} are hydrogens or C_{1-6}alkyls.

5. Derivative as defined in any one of claims 1, 2 or 4, characterized in that R_1 and R_2 are hydrogens.

6. Derivative as defined in claim 1, 2 or 4 - 5, characterized in that it has formula (III), where X is oxygen, one of groups R_3 and R_4 is a methyl group and the other is an α-alkene consistent with formula (II), where n + m + o equals 1 or 2 and R_1 - R_2 and R_5 - R_8 are hydrogens and R_9 - R_{11} are methyl groups.

7. Derivative as defined in claim 1, 2 or 4 - 5, characterized in that it has formula (IV), where X is oxygen, R_1 - R_4 are hydrogens, one of groups R_5 and R_6 is an α-alkene consistent with formula (II), where n + m + o equals 4, and R_9 - R_{11} are methyl groups.

8. Derivative as defined in claim 1 or 2, characterized in that one of groups R_9 - R_{11} is an α-alkene consistent with formula (II) and two of the groups are hydrogens or C_{1-6}alkyls, and R_3 - R_8 are hydrogens or C_{1-6}alkyls.

9. Derivative as defined in any one of claims 1, 2 or 8, characterized in that R_{10} and R_{11} are hydrogens or C_{1-6}alkyls, R_9 is an α-alkene consistent with formula (II), where n is 0 or 1, m is 0 or 1 and o is an integer 1 - 4 and R_1 - R_2 are hydrogens or C_{1-6}alkyls.

10. Derivative as defined in any one of claims 1, 2 or 8 - 9, characterized in that it has formula (III), X is oxygen, R_1 - R_4 and R_{10} - R_{11} are methyl groups, R_5 - R_8 are hydrogens and R_9 is an α-alkene consistent with formula (II), where n is 0, m is 1 and o is 3.

11. Derivative as defined in any one of claims 1, 2 or 8 - 9, characterized in that it has formula (III), X is oxygen, R_3 - R_4 and R_{10} - R_{11} are methyl groups, R_5 - R_8 are hydrogens and R_9 is an α-alkene consistent with formula (II), where m is 0 and o + n equals 1.

12. derivative as defined in claim 1 or 3, characterized in that one of groups R_9 - R_{11} is an α-alkene consistent with formula (II) and the other groups are hydrogens or C_{1-6}alkyls, and R_3 - R_8 are hydrogens or C_{1-6}alkyls or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 form a benzene ring together with the carbon atoms to which they are bonded.

13. Derivative as defined in any one of claims 1, 3 or 12, characterized in that R_{10} is an α-alkene consistent with formula (II) where n is 0 or 1, m is 0 or 1 and o is an integer 1 - 4 and R_1 and R_2 are methyl groups, R_9 is a C_{1-6}alkyl, R_{11} is a hydrogen, R_7 and R_8 are together an oxygen atom and R_4 and R_5, together with the carbon atoms to which they are bonded, form a benzene ring.

14. Derivative as defined in any one of claims 1 - 13, characterized in that it is 6-hydroxy-2,5,7,8-tetramethyl-2-(but-3-enyl)-chromane, 6-hydroxy-2,5,7,8-tetramethyl-2-(prop-2-enyl)-chromane, 6-hydroxy-2,2,7,8-tetramethyl-5-(1,1-dimethyl-hex-5-enyl)-chromane, 6-hydroxy-2,2,7,8-tetramethyl-5-(prop-2-enyl)-chromane, 5-hydroxy-4,6,7-trimethyl-3-(hex-5-enyl)-benzofurane or a hydroxythioxanthone derivative.

15. Method for producing an E-vitamin derivative or a compound analogous with it, which has the formula (Ia), characterized in that

(A) a hydroquinone derivative is allowed to react with a suitable unsaturated alcohol or thiol, or

(B) a hydroquinone derivative is allowed to react with a suitable unsaturated alcohol or thiol and an α-alkylene is added to the fused heterocyclic derivative thus formed.

16. Use of an E-vitamin derivative or a compound analogous with it, having the formula I

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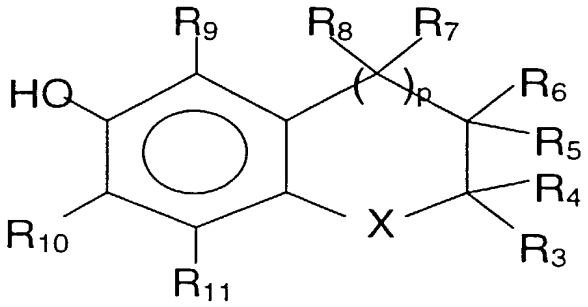

(I)

where X is an oxygen or sulfur atom, p is an integer 0 or 1, and R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II)

$$-(CH_2)_n-(CR_1R_2)_m-(CH_2)_o-CH=CH_2 \qquad (II)$$

where n, m and o are integers 0 - 4 independent of each other and R_1 and R_2 are identical or different groups selected from hydrogen or C_{1-6}alkyl or C_{1-6}alkene, which may be substituted with an aromatic ring,
or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene
as a stabilizing comonomer for the production of stabilized copolymer.

17. Stabilized copolymer, comprising at least one monomer variety, which is an olefin and/or a cyclic and/or aromatic compound containing an α-alkene chain, and a stabilizing comonomer, characterized in that the comonomer is an E-vitamin derivative or a compound analogous with it, which has the formula (I)

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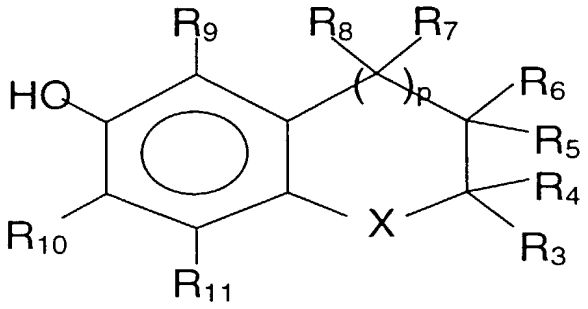


(I)

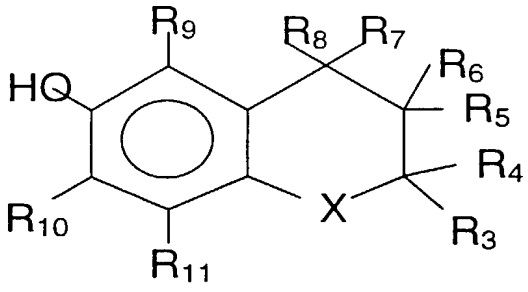
where X is an oxygen or sulfur atom, p is an integer 0 or 1, and R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II)

$$-(CH_2)_n-(CR_1R_2)_m-(CH_2)_o-CH=CH_2 \qquad (II)$$

where n, m and o are integers 0 - 4 independent of each other and R_1 and R_2 are identical or different groups selected from hydrogen or C_{1-6}alkyl or C_{1-6}alkene, which may be substituted with an aromatic ring,

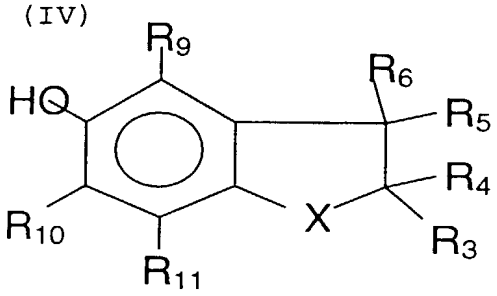
or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene.

18. Stabilized copolymer as defined in claim 17, characterized in that the comonomer has the formula (III)



(III)

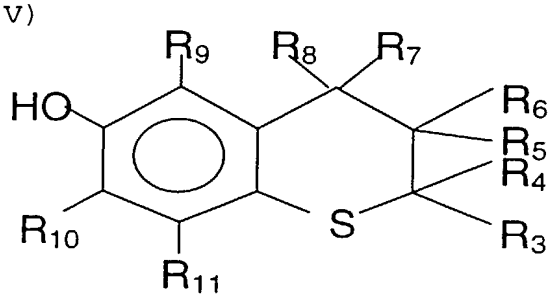
or the formula (IV)



(IV)

where X is an oxygen or sulfur atom and R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II).

19. Stabilized copolymer as defined in claim 17, characterized in that the comonomer has the formula (V)



(V)

where R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having the formula (II),

or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene.

20. Stabilized copolymer as defined in any one of claims 17 - 19, characterized in that the olefin is ethylene, propylene, butylene and/or pentene.

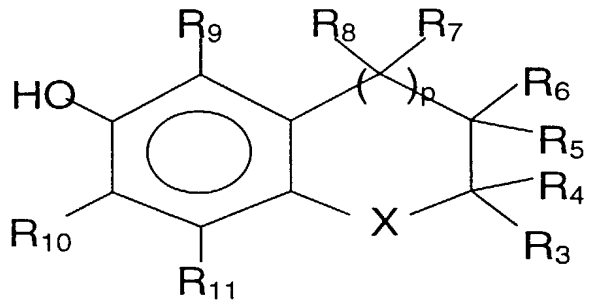
21. Stabilized copolymer as defined in any one of claims 17 - 20, characterized in that the the aromatic compound is styrene.

22. Stabilized copolymer as defined in any one of claims 17 - 21, characterized in that the copolymer consists of one olefin or styrene mono-

mer and comonomer consistent with formula (III), (IV) or (V).

23. Stabilized copolymer as defined in any one of claims 17 - 22, characterized in that the copolymer has a substantially regular structure.

24. Method for the production of stabilized copolymer, wherein at least one monomer variety, which is an olefin and/or a cyclic and/or aromatic compound containing an α-alkene chain, and a stabilizing comonomer are copolymerized in the presence of a catalyst by a polymerization technique known in itself, characterized in that the comonomer used is an E-vitamin derivative or a compound analogous with it, having the formula (I)



(I)

where X is an oxygen or sulfur atom, p is an integer 0 or 1, and R_3 - R_{11} are identical or different groups selected from the set hydrogen, C_{1-6}alkyl or α-alkene having the formula (II)

$$-(CH_2)_n-(CR_1R_2)_m-(CH_2)_o-CH=CH_2 \qquad (II)$$

where n, m and o are integers 0 - 4 independent of each other and R_1 and R_2 are identical or different groups selected from hydrogen or C_{1-6}alkyl or C_{1-6}alkene, which may be substituted with an aromatic ring,

or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene

ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene.

25. Method as defined in claim 24, characterized in that the comonomer used is a comonomer consistent with formula (III), (IV) or (V).

26. Method as defined in claim 24 or 25, characterized in that the copolymerization is performed using a metallocene catalyst or its derivative.

27. Method as defined in any one of claims 24 - 26, characterized in that the catalyst used in copolymerization contains a π-cyclo-pentadienyl transition metal compound and an alumoxane compound.

28. Method as defined in any one of claims 24 - 27, characterized in that the catalyst used in copolymerization contains a π-cyclo-pentadienyl transition metal compound and a compound containing boron.

29. Method as defined in any one of claims 24 - 28, characterized in that the comonomer has been complexed to the catalyst.

30. Method as defined in any one of claims 24 - 29, characterized in that the olefin is ethylen, propylene, butylene and/or pentene.

31. Method as defined in any one of claims 24 - 30, characterized in that the aromatic compound is styrene.

32. Method as defined in any one of claims 24 - 31, characterized in that the amount of monomer and stabilizing comonomer supplied into the process is exactly defined.

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
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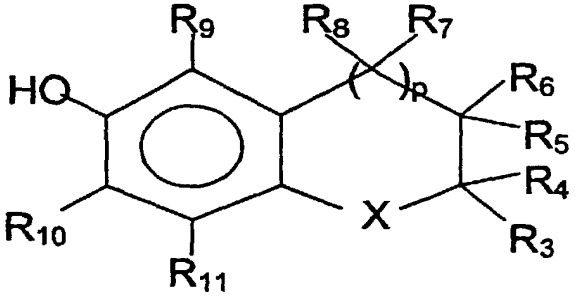
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A COMONOMER, AND A POLYMER STABILIZED WITH IT DURING POLYMERIZATION



(I)

$$-(CH_2)_n-(CR_1R_2)_m-(CH_2)_o-CH=CH_2 \qquad (II)$$

(57) Abstract: The invention concerns an E-vitamin derivative or a compound analogous with it, having formula (I), where X is an oxygen or sulfur atom, p is an integer 0 or 1, and R_3 - R_{11} are identical or different groups selected from hydrogen, C_{1-6}alkyl or α-alkene having formula (II), where n, m and o are integers 0 - 4 independent of each other and R_1 and R_2 are identical or different groups selected from hydrogen or C_{1-6}alkyl or C_{1-6}alkene, which may be substituted with an aromatic ring, or R_7 and R_8 are together an oxygen atom and/or R_4 and R_5 and/or R_{10} and R_{11} form together with the carbon atoms to which they are bonded a benzene ring, which may be substituted with groups selected from hydrogen, C_{1-6}alkyl or α-alkene. The invention also concerns the use of a derivative consistent with formula (I) as a stabilizing comonomer, and a stabilized copolymer and a method for the production of a stabilized copolymer.

WO 01/05781 A1

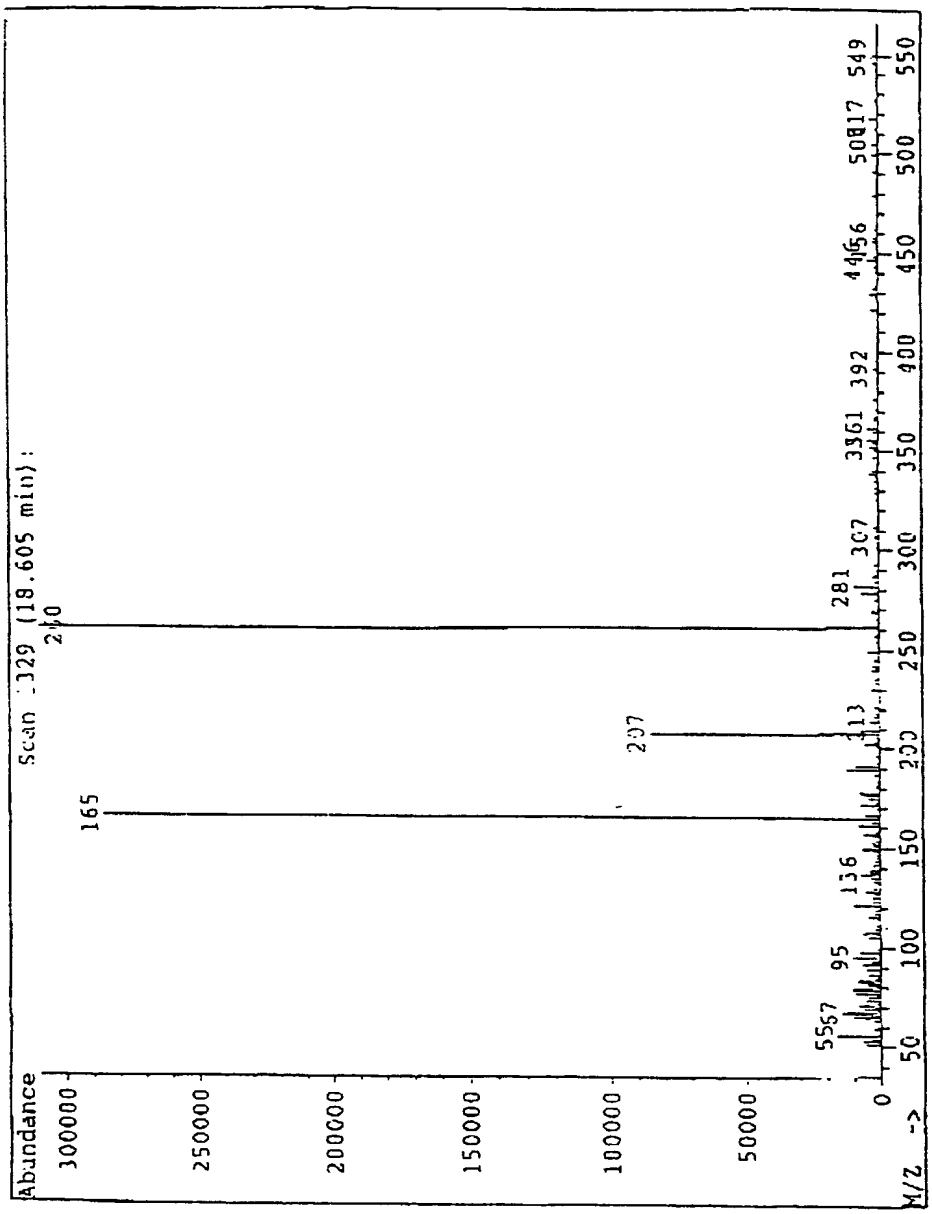

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Fig. 1

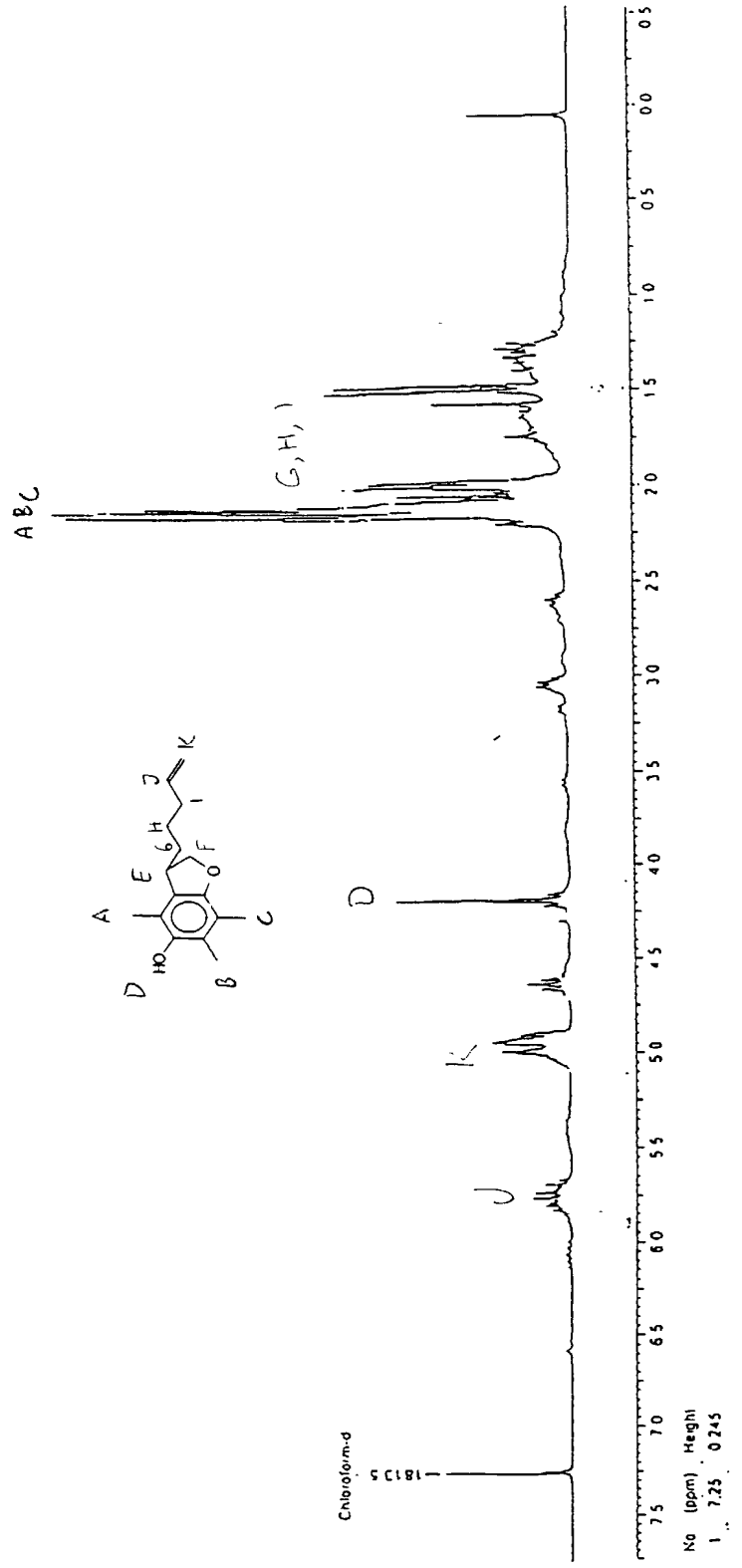
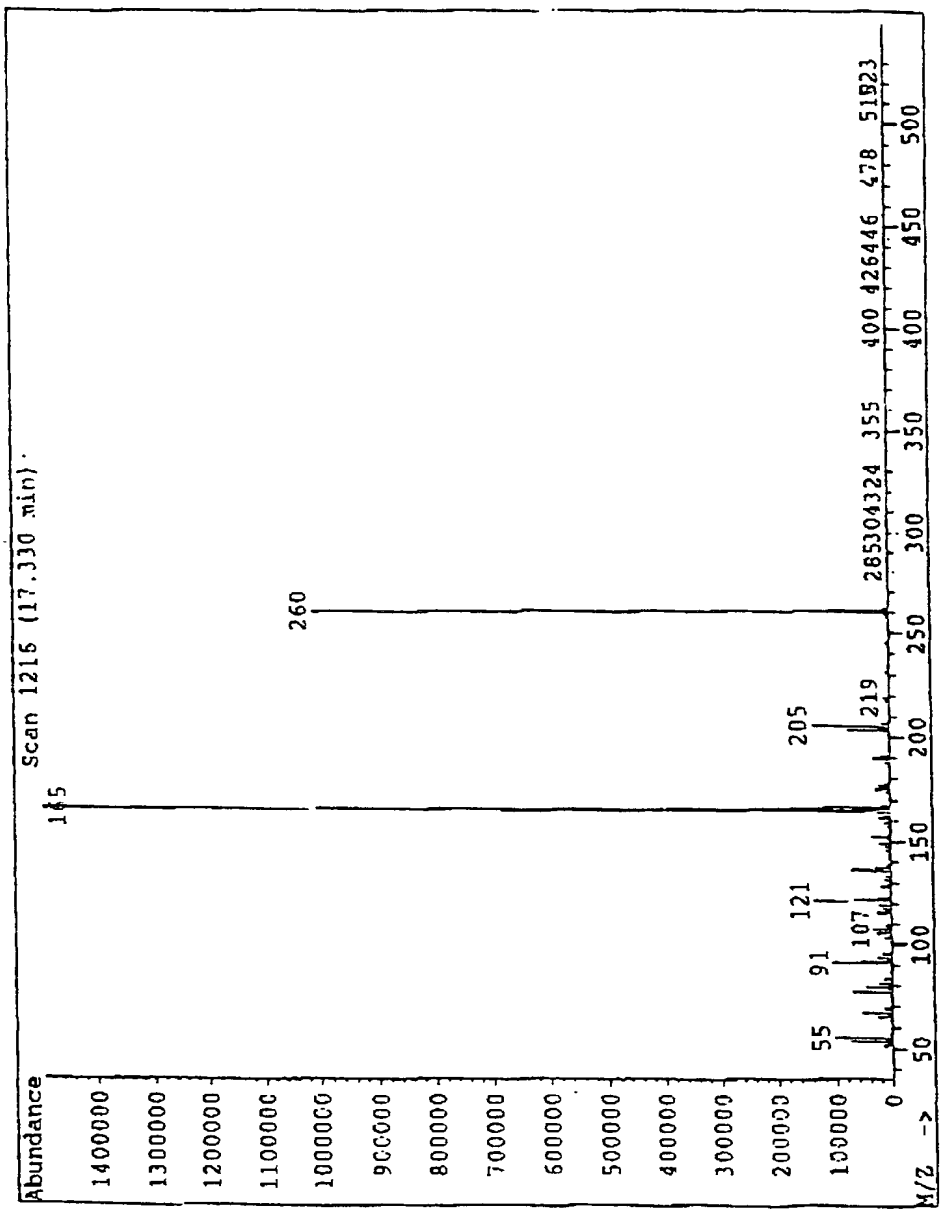


Fig. 2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50
100
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250
300
350
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450
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107
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165
205
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400 426446
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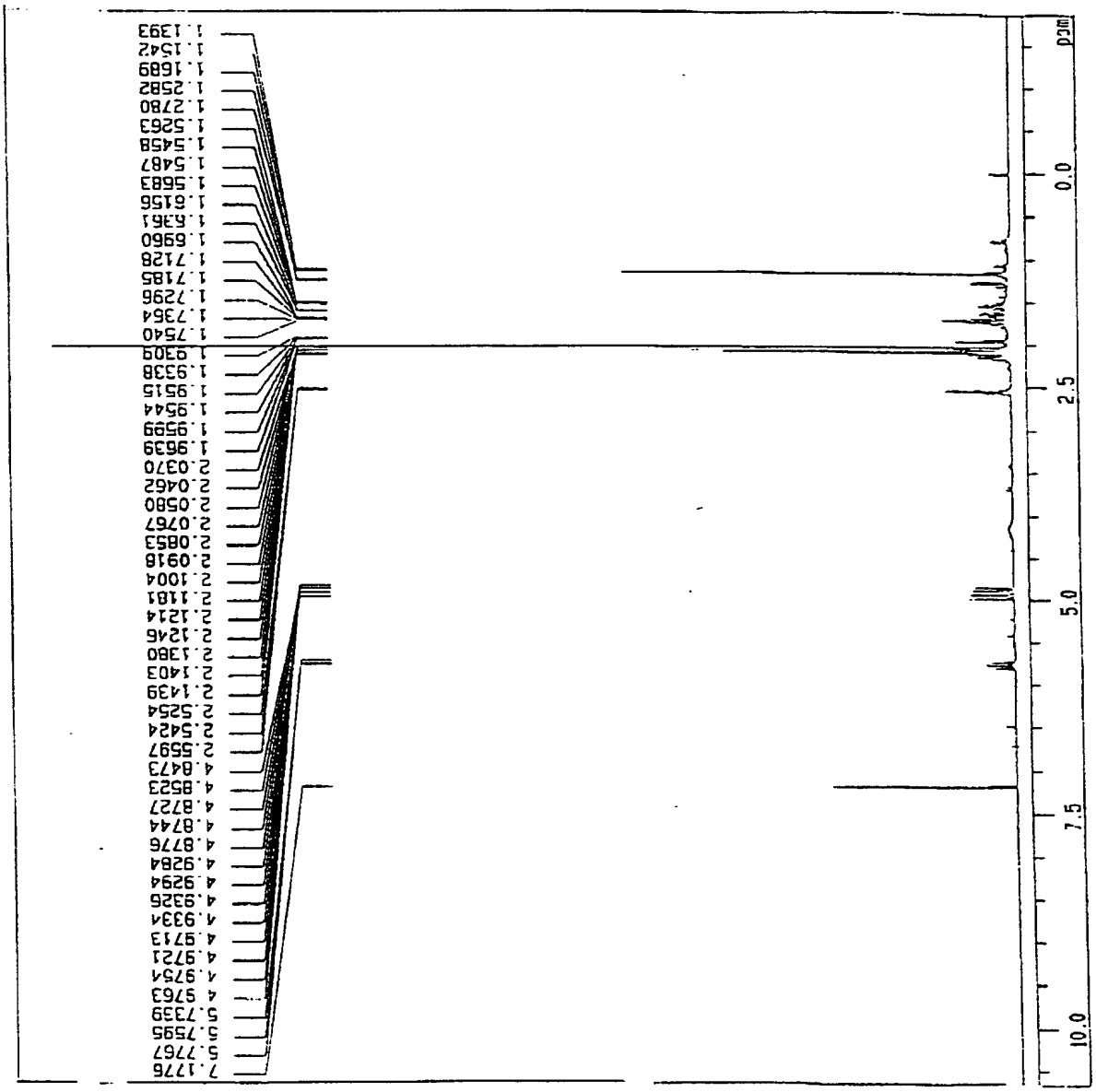
51823

Fig. 3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2.5254
2.5424
2.5597
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4.9294
4.9326
4.9334
4.9713
4.9721
4.9754
4.9763
5.7339
5.7595
5.7767
7.1776
ppm
0.0
2.5
5.0
7.5
10.0

Fig. 4

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PTO/SB/01
(8/96)

DECLARATION

Declaration ☐ Submitted with Initial Filing OR Declaration ☒ Submitted after Initial Filing

Attorney Docket Number	2534-00066
First Named Inventor	Auer, Markku
COMPLETE IF KNOWN	
Application Number	10/031,739
Filing Date	
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

A COMONOMER, AND A POLYMER STABILIZED WITH IT DURING POLYMERIZATION

(Title of the Invention)

the specification of which
☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) 06/28/2000 as United States Application Number or PCT International Number PCT/FI00/00585 and was amended on (MM/DD/YY) 08/15/2001 (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designed at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Copy Attached? YES	Copy Attached? NO
991634	Finland	07/21/1999	☒	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐
			☐	☐	☐

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	Additional provisional
		☐ Application numbers are listed on a supplemental priority sheet attached hereto.

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DECLARATION

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designated the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States of PCT International application in the manner provided by the first paragraph of Title 35, United States Code §112. I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

Name	Registration Number	Name	Registration Number
Glenn O. Starke	17,031	Edward R. Williams, Jr.	36,057
Eugene R. Sawall	17,431	Joseph D. Kuborn	40,689
Daniel D. Fetterley	20,323	William L. Falk	27,709
George H. Solveson	25,927		
Gary A. Essmann	29,376		
Thomas M. Wozny	28,922		
Michael E. Taken	28,120		
Joseph J. Jochman, Jr.	25,058		
Andrew S. McConnell	32,272		

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

☒ Please direct all correspondence to:	Name	Daniel D. Fetterley					
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City	Milwaukee	State	Wisconsin		Zip	53202-4178	
Country	United States	Telephone	(414) 271-7590		Fax	(414) 271-5770	

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name (first and middle [if any])	Family Name or Surname
Markku	Auer

Inventor's Signature					Date		
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POST OFFICE ADDRESS	VTT Kemiantekniikka, Biologinkuja 7						
City	Espoo	State		Zip	FIN-02150	Country	Finland

☒ Additional inventors are being named on supplemental sheet(s) attached hereto.

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DECLARATION	ADDITIONAL INVENTOR(S) Supplemental Sheet

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])				Family Name or Surname			
Carl-Erik				Wilen			
X Inventor's Signature				Date			
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POST OFFICE ADDRESS	Åbo Akademi, Teknisk Polymerkemi, Biskopsgatan						
City	Åbo	State		Zip	FIN-20500	Country	Finland

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])				Family Name or Surname			
Juha				Stranden			
X Inventor's Signature				Date			
RESIDENCE: City	Åbo	State		Country	FI	Citizenship	FI
POST OFFICE ADDRESS	Åbo Akademi, Teknisk Polymerkemi, Biskopsgatan						
City	Åbo	State		Zip	FIN-20500	Country	Finland

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])				Family Name or Surname			
Ari				Rosling			
X Inventor's Signature				Date			
RESIDENCE: City	Åbo	State		Country	FI	Citizenship	FI
POST OFFICE ADDRESS	Åbo Akademi, Teknisk Polymerkemi, Biskopsgatan						
City	Åbo	State		Zip	FIN-20500	Country	Finland

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])				Family Name or Surname			
300 Jan				Näsman			
X Inventor's Signature	psta Rune Näsman			Date	7/6 2002		
RESIDENCE: City	Åbo FIX	State		Country	FI	Citizenship	FI
POST OFFICE ADDRESS	Dragonvägen 58 b A 6						
City	Åbo	State		Zip	FIN-20700	Country	Finland

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])				Family Name or Surname			
Hendrik				Luttikhedde			
X Inventor's Signature				Date			
RESIDENCE: City	Turku	State		Country	FI	Citizenship	NL
POST OFFICE ADDRESS	Sirkkalankatu 27 A 28						
City	Turku	State		Zip	FIN-20700	Country	Finland

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			☐	☐	☐
			☐	☐	☐

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Application Number(s)	Filing Date (MM/DD/YYYY)	
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Daniel D. Fetterley	20,323	William L. Falk	27,709
George H. Solveson	25,927		
Gary A. Essmann	29,376		
Thomas M. Wozny	28,922		
Michael E. Taken	28,120		
Joseph J. Jochman, Jr.	25,058		
Andrew S. McConnell	32,272		

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

☒ Please direct all correspondence to:	Name	Daniel D. Fetterley			
Address	Andrus, Sceales, Starke & Sawall, LLP				
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City	Milwaukee	State	Wisconsin	Zip	53202-4178
Country	United States	Telephone	(414) 271-7590	Fax	(414) 271-5770

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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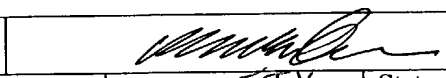
Given Name (first and middle [if any])	Family Name or Surname
Markku	Auer

Inventor's Signature					Date	Jan 14, 2002	
RESIDENCE: City	Espoo FIX	State		Country	FI	Citizenship	FI
POST OFFICE ADDRESS	VTT Kemiantekniikka, Biologinkuja 7, FIN-02150 Espoo						
City	Espoo	State		Zip	FIN-02150	Country	Finland

☒ Additional inventors are being named on supplemental sheet(s) attached hereto.

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DECLARATION	ADDITIONAL INVENTOR(S) Supplemental Sheet

200

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])			Family Name or Surname				
Carl-Erik			Wilen				
Inventor's Signature				Date	24 Jan 2002		
RESIDENCE: City	Åbo FIX	State		Country	FI	Citizenship	FI
POST OFFICE ADDRESS	Åbo Akademi, Teknisk Polymerkemi, Biskopsgatan						
City	Åbo	State		Zip	FIN-20500	Country	Finland

300

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])			Family Name or Surname				
Juha			Stranden				
Inventor's Signature				Date	7 May 2002		
RESIDENCE: City	Åbo FIX	State		Country	FI	Citizenship	FI
POST OFFICE ADDRESS	Åbo Akademi, Teknisk Polymerkemi, Biskopsgatan						
City	Åbo	State		Zip	FIN-20500	Country	Finland

400

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])			Family Name or Surname				
Ari			Rösling				
Inventor's Signature				Date	29 Jan 2002		
RESIDENCE: City	Åbo FIX	State		Country	FI	Citizenship	FI
POST OFFICE ADDRESS	Åbo Akademi, Teknisk Polymerkemi, Biskopsgatan						
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Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])			Family Name or Surname				
Jan			Näsman				
Inventor's Signature				Date			
RESIDENCE: City	Åbo	State		Country	FI	Citizenship	FI
POST OFFICE ADDRESS	Dragonvägen 58 b A 6						
City	Åbo	State		Zip	FIN-20700	Country	Finland

600

Name of Additional Joint Inventor, if any:	☐ A petition has been filed for this unsigned inventor						
Given Name (first and middle [if any])			Family Name or Surname				
Hendrik			Luttikhedde				
Inventor's Signature				Date	6 Feb 2002		
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